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Original article

Gamma irradiation for Cultural Heritage conservation: Comparison of the side effects on new and old paper

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ABSTRACT

Ionizing radiations, commonly applied as diagnostic tools in Cultural Heritage (CH) field, are also proving effective for eliminating biodeteriogens (insects, fungi, bacteria and molds) responsible for the degradation of CH artifacts and often harmful for restorers, archivists and librarians. The use of ionizing radiations, such as gamma rays, for CH treatments is spreading in many countries. However, some CH operators remain resistant due to insufficient knowledge about the potential physico-chemical modifications (secondary effects) induced by radiation. This work aims to investigate and compare the effects of irradiation parameters (such as absorbed dose and dose rate) on old paper samples and new pure-cellulose paper, chosen as a reference model material. Absorbed doses up to 8 kGy have been used, as these values are commonly agreed upon for the preservation treatment of CH artifacts and are generally effective for biodeteriogens removal. Optimizing irradiation conditions helps to minimize secondary effects (such as oxidation, depolymerization or color changes), thereby increasing the reliability of the process and boosting confidence among CH operators. The secondary effects were analyzed using various physico-chemical characterizations (Fourier Transform Infrared spectroscopy, Raman microscopy, viscosimetric and colorimetric analysis) on old and new paper samples. The results indicate varying behaviors, correlated with paper composition, sample age and irradiation parameters, towards gamma radiation. This groundbreaking study not only confirms the efficacy of gamma irradiation treatments but also provides essential data that will aid in the development of optimized best practice protocols and guidelines for non-destructive and minimally destructive methods applied to real case studies and treatments.

1. Introduction

The preservation of world Cultural Heritage (CH) is crucial for conserving cultural traditions and national identities. CH artifacts are often threatened by biodeteriorating agents, such as microorganisms (fungi, molds, bacteria), insect pests or lichens which can cause severe physical and chemical damages, leading to the degradation of CH materials and posing health risks to restorers, archivists and operators. Artifacts made from natural materials (such as paper, parchment, leather, textiles, and wood) are particularly vulnerable to biodegradation [1,2]. Ionizing radiations, including gamma rays, electrons, and X-rays, offer an effective solution for eradicating insects and removing microorganisms from degraded archived materials or CH artifacts [3–6]. These methods are preferred over alternatives like ethylene oxide and chemical fumigation, which can leave harmful residues and pose risks to operators. Freeze-drying and anoxic treatments are limited in their microbial effectiveness. Radiation technology, used since the 1960s, has been internationally evaluated by IAEA institutions for decontamination [5,7–12]. Gamma radiation, in particular, offers several advantages: it enables the rapid processing of numerous objects and penetrates deeply into multi-component and complex-shaped artifacts, ensuring simultaneous treatment of both the surface and bulk. Despite these clear advantages over traditional recovery methods, the interaction of ionizing radiation with the arti-

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fact materials can lead to potential changes (or secondary effects) in their structure, chemical composition or appearance. Given the uniqueness of CH objects, even minimal modifications induced by conservation treatments may be deemed acceptable to avoid losing the artifact. Understanding radiation-induced secondary effects, which vary based on irradiation parameters and material properties, is crucial for advancing the use of this technology. Reliable, specific scientific results from non-invasive and minimally destructive techniques are essential for the CH community.

Secondary effects of gamma radiation can be classified as direct (occurring during irradiation and dependent on the absorbed dose) or indirect (occurring post-irradiation and related to chemical reactions involving free radicals produced during treatment) [13–15]. These effects include changes in the structural network (crosslinking or chemical bond degradation at low and high doses, respectively), oxidation reactions, and material-humidity interactions, which can manifest as macroscopic alterations like color changes or loss of mechanical properties [16–18].

The recommended dose range for CH conservation treatment is 8 ± 2 kGy [12]. In this study, gamma irradiation was applied with absorbed doses up to 8 kGy, sufficient for biodeteriogens eradication, as confirmed by microbiological analysis. Irradiation tests were performed at two dose rates (130 Gy/h and 1500 Gy/h), representing different magnitudes commonly available in irradiation facilities. The samples of interest were investigated before and after irradiation using various experimental techniques to achieve a comprehensive physico-chemical characterization. To facilitate comparison of results across different laboratories and to address the needs of the cultural heritage community, we selected non-invasive and minimally destructive techniques that are commonly used [19]. Raman microscopy and infrared spectroscopy were employed to assess the morphology, molecular structure and conservation state of the papers, while viscosimetric measurements were used to evaluate their Degree of Polymerization (DP). Additionally, colorimetric analysis was performed to measure color changes induced by the irradiation treatments.

The results of this study not only clarify the effects of irradiation parameters on minimizing secondary effects but also confirm the efficacy of gamma irradiation treatments. The introduction of adaptable irradiation and characterization protocols for entire CH objects represents a groundbreaking approach in the field. This innovative methodology provides a more comprehensive and effective framework for preservation, offering valuable data that will aid in developing optimal strategies and criteria for conserving cultural heritage artifacts.

2. Research aim

This work investigates the specific secondary effects induced by gamma radiation treatment on different types of paper for conservation purposes, at absorbed doses up to 8 kGy (a subject not widely treated extensively covered in the literature). The study includes a comparison of the results obtained from irradiating a new reference model paper (already studied in our previous works [13,14,20]) with two old books provided by the National and University Library of Zagreb (Croatia). This comparison is crucial due to the significant variability in paper composition, which can influence how radiation interacts with the paper and affect the final properties of paper-based products [3,4,13,21–23]. Although paper documents are primarily composed of cellulose, they often contain other materials such as lignin, hemicelluloses, organic entities, and mineral constituents. The content of these materials varies depending on the papermaking process, paper type, and production period [24,25]. Another critical aspect is the irradiation parameters, such as dose rate and absorbed dose, which can significantly impact the extent of the secondary effects.

3. Materials and methods

3.1. Samples preparation

Two books provided by the Croatian National and University Library (NUL) of Zagreb ("Monistische Sonntagspredigten" of Wilhelm Ostwald, 1911; "Die Elemente Der Metaphysik" of Dr. Paul Deussen, 1890) were used for the analysis and irradiation tests described in the present paper. Whatman paper No. 1 (thickness = 0.20 mm, Carlo Erba, Italy), extensively studied in our previous papers [13,14], was chosen as the reference model material. As reported in Section 3.1, the composition of the analyzed papers is different, characterized by the presence of cellulose (Whatman paper and the older books) and of lignin (in the book dating back to 1911). The investigated ancient books, along with the representation of cellulose chains and lignin units, are shown in Fig. 1.

To obtain samples as homogeneous as possible, square pieces of 2 cm x 2 cm were cut from unprinted areas of the central pages of the books (details in the Supporting Information). Similarly, Whatman reference samples of the same size were used. The samples are labeled as "W" for Whatman paper, "D" for Deussen's book and "O" for Ostwald's book.

3.2. Gamma irradiation tests

The irradiation tests were performed at the Calliope gamma irradiation facility (ENEA Casaccia R.C., Rome, Italy) equipped with a ^{60}Co (mean energy of 1.25 MeV) radioisotopic source array [26].

The samples were irradiated in air, at room temperature and humidity conditions, at absorbed doses of 4 kGy and 8 kGy at two dose rates (130 Gy/h and 1500 Gy/h), which are commonly available in gamma irradiation facilities. All absorbed dose and dose rate values are referred to water. The dose rates were experimentally determined at the dosimetric laboratory of the Calliope facility, using Fricke and alanine-EPR dosimetric systems. The facility has also a characterization laboratory where various analyses were performed before and after irradiation tests. To ensure that any observed effects are accurately attributed to the irradiation, the characterization measurements were conducted immediately after irradiation for all samples.

3.3. Characterization techniques

Optical microscope images and Raman spectra of the samples were collected with a micro-Raman spectrometer (Horiba XploRA Plus). FTIR spectra were recorded using a Spectrum 100 Perkin-Elmer FT-IR spectrometer. Viscosity measurements were performed using a TA Instrument AR 2000 rheometer, following the procedure described in the ISO:5351:2012 standard regulation [27]. Colorimetric measurements were performed with a PCE-CSM 8 colorimeter according to the CIE 2000 system of colorimetry [28]. All measurements were conducted in air at room temperature and humidity. Further details are reported in the Supporting Information section.

4. Results and discussions

4.1. Preliminary microbiological tests

Before irradiation, microbiological sampling was performed on the old books to investigate the types of microbiological communities present on the samples. Microbial strains were sampled from selected areas of the books (cover and inner page, namely 1 and 2) where microorganisms were suspected to be present. The isolated strains were then streaked onto YPD (Yeast Extract Peptone Dextrose) agar plates to spread the microbial sample across the plate,

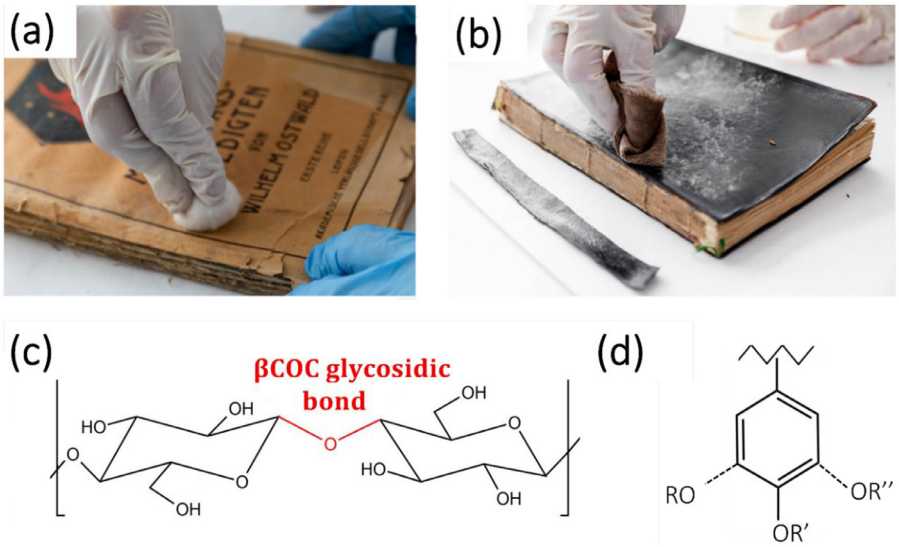

Fig. 1. Photo of (a) Ostwald's and (b) Deussen's authored books; schematic representation of (c) cellulose and (d) lignin units. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

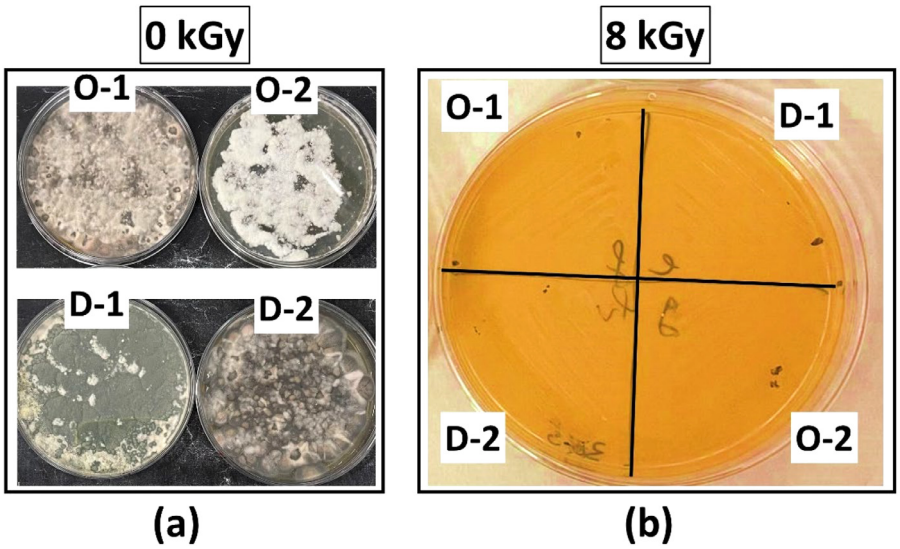

Fig. 2. Growth of the microbial community before (a) and after (b) irradiation at 8 kGy at the highest dose rate. The labels O-1, O-2, D-1 and D-2 indicate the sampled positions (1 and 2) for the O and D books.

allowing individual colonies to form. The YPD plates were kept at 28 °C for one week to promote the growth of the microorganisms. After this incubation period, the plates were examined to assess microbial growth. Subsequently, the plates were irradiated under different conditions, and the previously described steps (sampling and streaking on new YPD plates) were repeated to check for colony growth after one week. This process helped determine the most effective conditions for microbial removal, which were then applied for the irradiation of the old books.

As an example, Fig. 2 depicts the growth of the microbial community after one week, both before (Fig. 2a) and after irradiation at 8 kGy and 1.5 kGy/h (Fig. 2b). A complete eradication of the microbial communities is evident, providing clear evidence of the effectiveness of gamma radiation for CH preservation.

4.2. Samples before irradiation

Pictures and optical microscope images of reference Whatman paper (W samples) and of Ostwald and Deussen books pages (O and D samples) before irradiation are shown in Fig. 3.

Fig. 3a-b-c illustrates that the samples before irradiation exhibit distinct differences in appearance, coloration, and morphology, likely due to varying chemical compositions and degrees of aging of the three types of paper [29]. More detailed information is provided by the optical microscope analysis. The inset image in Fig. 3a shows that the surface of the reference W sample consists of fibrillar structures characteristic of cellulose chains. This observation is consistent with the chemical composition of this paper, which is composed of over 98 % cellulose. In contrast, the inset of Fig. 3b displays a compact morphology for the O sample, featuring well-organized structures indicative of paper with a high lignin content [30]. The inset of Fig. 3c, related to the D sample, closely resembles the morphology of the reference W sample.

To further investigate the structural characteristics of the three types of paper, Raman spectroscopy analyses were performed on each sample. The Raman spectra obtained from the samples before the irradiation are presented in Fig. 4.

In accordance with the morphological analysis, Fig. 4 shows that the Raman spectra acquired for the D and W samples exhibit signals attributable to cellulose (c) and hemicellulose (h) chains.

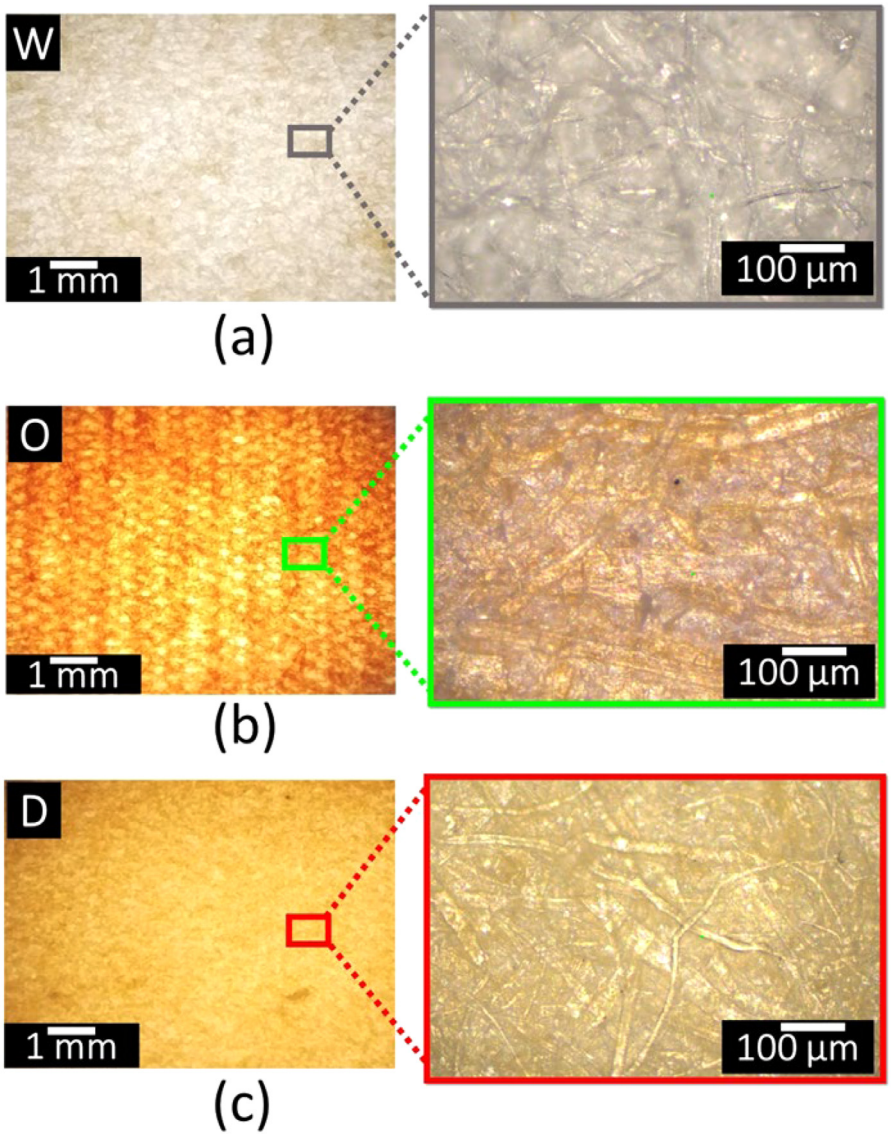

Fig. 3. Pictures (2.5X) of (a) W, (b) O and (c) D samples before gamma irradiation; insets: optical microscope images (magnitude 10X).

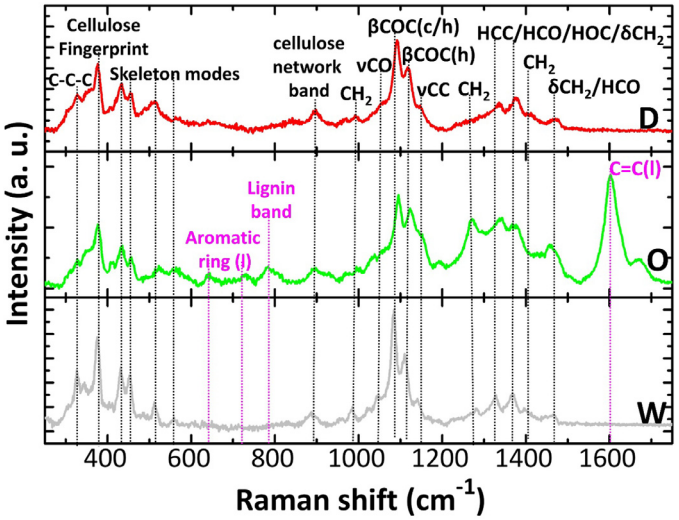

Fig. 4. Representative Raman spectra of O, D and W samples, with signals attribution. The labels indicate cellulose (c), hemicellulose (h) and lignin (l).

In contrast, the Raman spectrum for the O sample clearly displays additional peaks related to lignin (l) phases [31–41]. The spectra do not reveal any signals corresponding to fillers, foreign fibers or metallic impurities, indicating the absence of crystalline phases of additional substances. Further details are provided in the Supporting Information. Due to these observations, the Raman spectroscopy analysis confirms that the chemical composition of the D and W samples is highly similar, indicating a significant level of cellulose content in these types of paper. However, the peaks observed in the Raman spectrum of the D sample are broader compared to those of the W sample. Given that the D book was produced over 100 years ago, this evidence can reasonably be attributed to cellulose degradation resulting from the natural aging of the paper. In this context, the broadness of the peaks in the O samples spectrum suggests a significant degree of degradation and lower quality for the lignin-containing paper used to produce the O book. Additional information on the chemical composition of the investigated materials is provided by the ATR-FTIR measurements performed on the D, O and W samples, as detailed in Fig. 5.

In agreement with Raman spectroscopy analysis, all ATR-FTIR spectra in Fig. 5 exhibit bands at 1160 and 900 cm^{-1}, which are attributed to CO and COC functional groups [42–44]. However, only

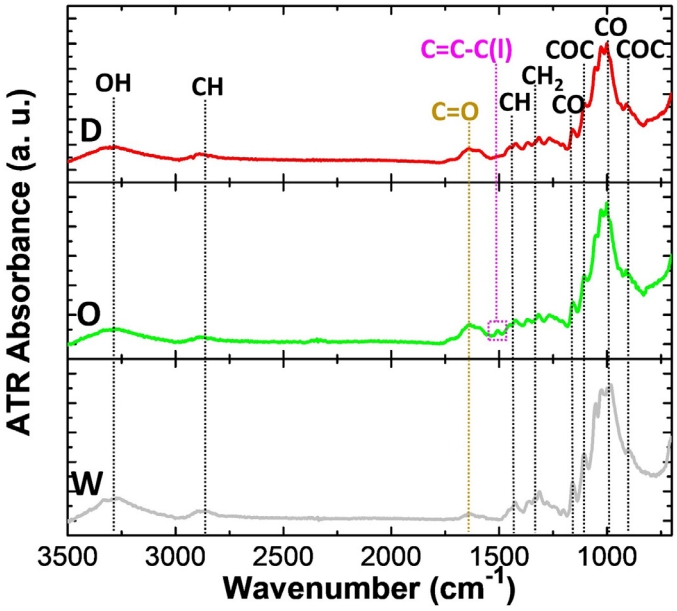

Fig. 5. Representative ATR spectra of D, O and W samples, with signals attribution. The labels indicate lignin (l).

the spectrum of the O sample shows a peak around 1510 cm^{-1}, indicative of the lignin component [45,46]. Additional bands characteristic of cellulose-based materials appear around 1000 and 1230 cm^{-1} (C–O stretching modes) and in the region of 1250–1380 cm^{-1} (CH_2 bending vibrations) [33,46,47]. The bands at approximately 1400, 1650 and 3300 cm^{-1} are assigned to C-H bending, C = O stretching and O–H stretching modes, respectively [46,47]. Further details about the samples features before irradiation are provided by the FTIR analysis in the spectral region between 1800 and 1525 cm^{-1}, as shown in Fig. 5, where signals related to adsorbed water (not studied in the present work) [13], carbonylic (C = O) and carboxylic (COO^-) moieties are present. To isolate the contribution of each signal, a multiple Gaussian fit and deconvolution procedure were performed. Since the peak areas are proportional to the amount of the related moieties, their analysis provides quantitative information specifically related to the oxidation degree (in terms of carbonylic and carboxylic groups) of the samples of interest. The representative deconvolved spectra for the samples before the irradiation tests are shown in Fig. 6.

From the spectra reported in Fig. 6, the presence of the adsorbed water molecules band (H_2O_{ads}) is evident at 1670 – 1630 cm^{-1}, showing similar characteristics across all samples. In terms of oxidation state, there is a noticeable difference: the W sample spectrum exhibits a negligible C = O stretching mode peak (1750 – 1710 cm^{-1}), while this contribution, which is proportional to the oxidation degree of the paper, is significantly more pronounced in the D sample and reaches its maximum in the O sample [48,49]. Additionally, a third peak attributed to the asymmetric stretching mode of COO^-(below 1630 cm^{-1}) appears only in the D and O samples, which is specifically related to their higher aging degree and/or possibly suboptimal conservation conditions with respect to light, temperature and relative humidity [50].

4.3. Samples after irradiation

The irradiation conditions used in this study resulted in a slight decrease in the Tensile Chemical Index (TCI), Lateral Order Index (LOI) while no modifications occur for Hydrogen Bonding Index (HBI) for W samples at gamma radiation doses up to 8 kGy. In contrast, these indices remained unchanged for the old paper samples after gamma irradiation, indicating that the applied doses do not compromise the physical or chemical properties of the old paper artifacts (details in the Supporting Information). The differences in the magnitude values of the indices for the various types of paper could be correlated with the extent of property modifications following irradiation. This means that the observed changes in TCI, LOI, and HBI are related to the degree to which each type of paper has been affected by the gamma irradiation process.

As discussed in the Introduction, the first point of investigation is the potential increase in the oxidation level of paper due to gamma radiation treatment and its dependence on irradiation parameters such as dose rate and absorbed dose values. To address this, FTIR spectra in the range 1800 – 1525 cm^{-1} were analyzed, following the methodology described in the previous section. The

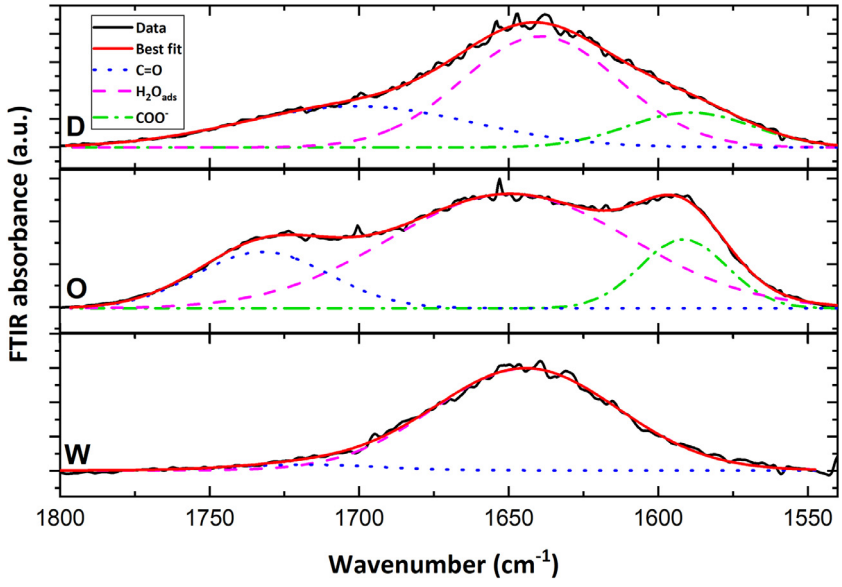

Fig. 6. FTIR spectra in the range 1800 – 1525 cm^{-1} for the D, O and W samples before the irradiation processes. The black lines represent the experimental data, the red lines are the best triple gaussian fits. The dashed lines correspond to the contributions of the C = O (blue), adsorbed water (magenta) and COO^- (green) peaks. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

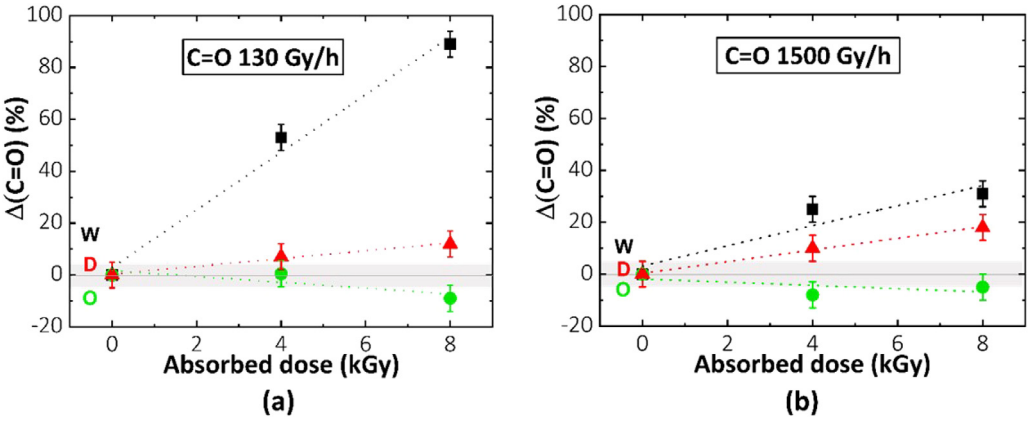

Fig. 7. Trend of the variation of C = O peak area values (relative to the measurements of the unirradiated samples) as a function of the absorbed dose at dose rates of (a) 130 Gy/h and (b) 1500 Gy/h for W (black squares), O (green dots) and D (red triangles) samples. The grey zones represent the Δ(C = O)% error (±5 %). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

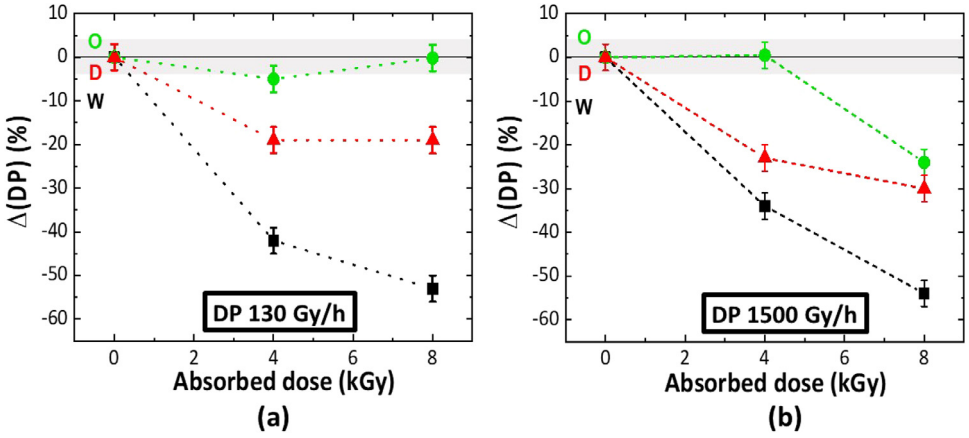

Fig. 8. Trend of the percentage variation in DP values (relative to the unirradiated samples) as a function of the absorbed dose at dose rates of (a) 130 Gy/h and (b) 1500 Gy/h for W (black squares), O (green circles) and D (red triangles) samples. The grey zones represent the Δ(C = O)% error (±4 %). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

experimental data indicate that the area of the COO^- peaks remains essentially constant for all samples, while the areas of the carbonylic group peaks vary with the irradiation parameters (Figure S1). In Figure S1, the C = O peak areas for the W, O and D samples are reported for each irradiation condition. Since the paper samples differ in thickness, the peak area values are normalized to account for this variation, allowing for accurate quantitative comparison. Before irradiation, the W, O and D papers were characterized by C = O peak areas normalized to the sample thickness, measuring approximately 20 mm^{-1}, 174 mm^{-1} and 90 mm^{-1}, respectively. This indicates that the W paper, being the newest, shows the lowest degree of oxidation. In contrast, the D paper, and even more so the O paper, show significantly larger C = O peak areas. Specifically, the D paper is approximately four times more oxidized than the W reference sample, while the O paper is around ten times more oxidized. The observed behavior can be attributed to both the age of the D and O samples and the influence of environmental conditions (temperature, light, relative humidity) during their conservation and storage [51,52]. The data for the irradiated samples at both dose rates show increasing trends, to varying extent, for the W and D papers, whereas no increase in carbonyl groups is observed for the O sample. Although the conservation conditions of the D and O books, which contribute to their initial oxidation degree (at 0 kGy), are unknown, the data in Figure S1 suggest that the lignin present in the O paper acts as a protective mechanism against radiation. Lignin, characterized by aromatic rings, may serve as a shield for cellulose at this stage of degradation, thereby limiting the formation of additional carbonyl bonds during the gamma irradiation process [45,53]. To better appreciate the effect of irradiation on the samples, the data are expressed in terms of the percentage variation of the C = O peak area, denoted as "Δ(C = O)%" (calculated relative to the C = O peak area of the unirradiated samples), and are reported in Fig. 7 for the different treatment conditions. This analysis provides a clearer and more quantitative assessment of the oxidation process attributed to gamma ray interaction with the paper cellulose network.

Fig. 7a-b shows a noticeable difference between the trends exhibited by the W paper and the old samples. The reference material (W) is characterized by a significant increase in the Δ(C = O)% parameter, especially at the lowest dose rate, as a function of the absorbed dose. Specifically, the oxidation marker increases by up to approximately 90 % for the W sample irradiated at 8 kGy and 130 Gy/h (Fig. 7a), whereas a more moderate increase (around 30 %) is observed at the same absorbed dose when the irradiation is conducted at the highest dose rate of 1500 kGy (Fig. 7b). This finding aligns with previous studies [13,14] and is likely due to the oxidative degradation mechanism, which results in fewer C = O bonds forming during shorter irradiation times when the radiation processing occurs in air.

In contrast, the old D and O samples display very similar trends and oxidation levels as a function of the absorbed dose, regardless of the dose rate. A slight increase in Δ(C = O)% is observed for the

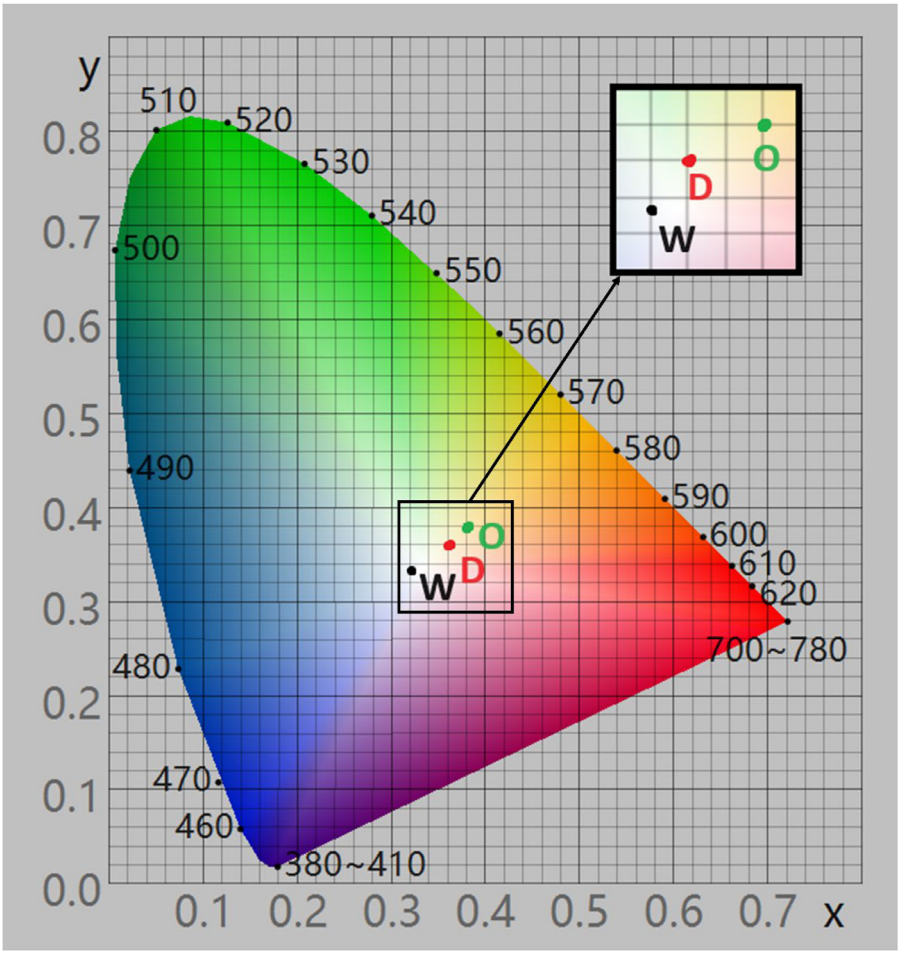

Fig. 9. The CIE XYZ color space chromaticity diagram for W (in black), D (in red) and O (in green) samples. The points correspond to the color coordinates of the samples before and after irradiation under different conditions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

D sample (without lignin) after irradiation at 8 kGy, but no significant changes are detected for lower doses, considering the experimental error (±5 %). The Δ(C = O)% trends for the old books at both low and high dose rates may be attributed to radicals recombination reactions.

In summary, the different behaviors observed for the investigated samples can be reasonably explained by their different age, conservation state and chemical composition. Specifically, the higher the initial oxidation level of a sample (present before irradiation), the fewer the sites available for further oxidation induced by radiation. Therefore, paper types with a significant amount of carbonyl (and carboxyl) groups are more stable and less susceptible to modification during gamma radiation exposure. The data also highlight that the chemical composition of paper is crucial for its radiation resistance, with lignin molecules providing a protective role. Consequently, the greater increase in C = O groups observed in the reference W sample under irradiation indicates its minimal aging and high cellulose content (no lignin present).

To validate the results obtained from the FTIR investigation and to gain insight into the polymerization degree of the samples, viscosity measurements were conducted before and after irradiation (details in Supporting Information). The DP is related to paper mechanical properties, such as tensile strength and brittleness, due to changes in the cellulose chemical bonds network. A significant decrease in DP is generally associated with paper degradation and a consequent loss of mechanical properties [54–57]. Thus, investigating changes in DP, potentially induced by radiation, is crucial for ensuring the preservation of paper's mechanical properties.

Additionally, as reported in the literature [58,59], it is useful to establish a threshold value for the degree of polymerization for old or valuable documents. Specifically, the DP should remain above 300 for safe handling [58], as this parameter is highly dependent on the conservation state of the material.At the same time, the conservation state of books or documents will influence the establishment of guidelines by librarians regarding their usability, handling and consultation procedures (i.e. public access or restricted consultation). Given the importance of the DP parameter for a comprehensive characterization of paper materials, this work measured the degree of polymerization for all samples of interest, both before and after irradiation at different conditions.

The DP value for the W paper before irradiation (approximately 1200) is 6–7 times higher than that of the old books before irradiation (approximately 170 for the O paper and 190 for the D paper). The DP values lower than 200 for the O and D books (before irradiation) can be attributed to improper storage conditions and natural aging processes. The results after irradiation are presented in Figure S2. To better understand the effects of radiation treatment on the different papers, the percentage variation in DP (relative to the initial state of the samples at 0 kGy) at different absorbed doses and dose rates is reported for all investigated samples in Fig. 8.

A common trend is observed for the W and D samples, with a reduction in DP as a function of the absorbed dose. However,

Table 1
ΔE_{00} values of samples W, O and D after irradiation (ΔE_{00} relative to the corresponding unirradiated initial states of each sample). Error: ±1 %.

Sample	Absorbed dose (kGy)	Dose rate (Gy/h)	ΔE_{00}
Whatman paper (W)	4	130	0.36
	8		0.42
	4	1500	0.78
	8		0.82
Ostwald book (O)	4	130	0.58
	8		0.88
	4	1500	1.37
	8		1.37
Deussen book (D)	4	130	1.17
	8		1.19
	4	1500	1.69
	8		1.62

there is a significant quantitative difference between them: the DP of the W paper is reduced by approximately 43 % and 33 % at 4 kGy for the lower and higher dose rates, respectively. At the highest dose of 8 kGy, the DP further decreases by 50 % to 60 %, regardless of the dose rate. As depicted in Fig. 8, gamma exposure results in modest or negligible variation in the DP values for the O sample, with a maximum DP loss of about 24 % observed after irradiation at 8 kGy and a dose rate of 1500 Gy/h. Sample D exhibits the greatest DP decrease (30 %) at the highest dose rate and absorbed dose, while a smaller loss of 20 % is noted at the lowest dose rate.

The data suggest that, especially for aged samples, the choice of the irradiation dose rate is crucial for minimizing the DP reduction. Even in the worst-case scenario, the DP of the aged samples does not decrease by more than 30 % from the initial value, which translates in a high remaining percentage of the tensile index [60], suggesting that the treatment at these conditions does not significantly alter the mechanical properties of the paper. Consistent with our previous publication [13], the best results for the new W paper are achieved with higher dose rates. Nevertheless, even in the most adverse conditions, the DP remains above the threshold value of 300, ensuring the preservation of the paper's utility properties.

Among the possible radiation-induced secondary effects, color modification (such as yellowing or, in more severe cases, browning) is a major concern for CH operators. This feature, which is directly related to the paper oxidation state, is significantly influenced by the material's aging and its environmental conservation conditions.

To assess color changes, colorimetric analyses were performed on each sample before and after irradiation. The color change is quantified using the ΔE_{00} value, which represents the chromatic difference between two samples, as described in the Supporting Information [28,61–65], based on the CIE 2000 color system. The color of the samples is represented in the CIE XYZ color space chromaticity diagram. Specifically, in this space, a color is depicted as a point, as illustrated in Fig. 9.

The ΔE_{00} values for W, O and D samples at their initial state (ΔE_{00} values at 0 kGy relative to the white reference standard) are as follows: $\Delta E_{00} = 1.12$ for W, $\Delta E_{00} = 18.3$ for O and $\Delta E_{00} = 12.5$ for D. The ΔE_{00} values measured after irradiation at various conditions (ΔE_{00} values relative to the corresponding unirradiated samples) are reported in Table 1.

Regarding the data before irradiation, there is a significant difference in the ΔE_{00} values between the new W paper and the old books. The increase in paper yellowing follows the order W, D, and finally O, which aligns with the FTIR spectra findings, reflecting the increase in oxidation levels of the samples. This color change is a macroscopic consequences of the oxidation process itself.

Despite the inherent color differences among the types of paper, the results indicate that although slight ΔE_{00} increases occur with higher absorbed doses, no perceptible color difference is noticeable to the naked eye in any irradiated samples compared to their initial state, with ΔE_{00} always remaining below 1.8 [64,66,67].

5. Conclusions

The present work investigates the effects of gamma irradiation parameters (absorbed dose and dose rate) on papers of different compositions and conservation states using various physicochemical characterization techniques. Specifically, new Whatman paper (made of pure cellulose and chosen as a reference material) and two books from the late 1800s (D book) and early 1900s (O book, containing lignin phase) were analyzed before and after gamma irradiation treatment within the common absorbed dose range (up to 8 kGy) used for disinfecting bio-deteriorated cultural heritage artifacts. The results indicate that the behavior under irradiation depends on the initial oxidation degree of the samples and their structural and chemical composition.

The newest Whatman paper is more sensitive to gamma treatment effects, exhibiting higher oxidation and depolymerization degrees as a function of the absorbed dose. Conversely, the already oxidized old books are modified to a lesser extent, with the protective action of the lignin group evident in the O book from 1911. This behavior can be explained by the higher number of oxidation sites available in the Whatman paper compared to the naturally oxidized old papers. Interestingly, the findings may indicate that deteriorated cellulose papers are more resistant to irradiation than contemporary ones.

Regarding the dose rate effect, while the results for Whatman paper confirmed those found in our previous work and described in the literature, in terms of oxidative degradation process resulting in more pronounced modifications at lower dose rates, the old books showed an opposite trend, likely due to competitive radical reactions. Despite the measured modifications, none were significant enough to cause perceptible paper yellowing or loss of mechanical properties in the papers.

In conclusion, the experimental results obtained in this work provide conclusive evidence of the impact of gamma irradiation parameters (absorbed dose and dose rate) on different types of paper when used for CH conservation purposes. These results may guide the selection of doses for similar objects with comparable bioburden levels without requiring a destructive approach, based on prior evaluations of dose effects. However, further research is necessary to validate these results even more, given the vast quantity of old paper that exists.

The study demonstrates the possibility of controlling and minimizing the secondary effects induced by radiation, making gamma irradiation a very promising and useful method for the conservation of biodeteriorated CH artifacts of natural origin. This advanced approach not only demonstrates the effectiveness of gamma irradiation but also paves the way for developing optimal methodologies and standards, thereby revolutionizing the preservation techniques used in cultural heritage conservation.

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Supplementary materials

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